

Patterned Dye Diffusion using Transferred Photoresist for Polymer OLED Displays

Florian Pschenitzka and J. C. Sturm

Department of Electrical Engineering, Center for Photonics and Optoelectronic Materials (POEM), Princeton University, Princeton, NJ 08544, USA

ABSTRACT

A method of large-area dye diffusion for patterning the emissive color of organic light-emitting devices (OLEDs) using transferred photoresist is introduced. Using a large-area dye diffusion source, the dye is diffused into the emissive layer of the OLED. To locally pattern the emissive color, either a shadow mask or a patterned dye source has to be used. The implementation of both approaches using photolithographic patterning and transferred photoresist is outlined in this paper. In addition, a method using transferred photoresist for patterning of the cathode will be discussed.

INTRODUCTION

Recent improvements in polymer organic light-emitting diodes (OLED) efficiency with low turn-on voltages¹⁻³ have fostered the prospect of commercial applications of polymer OLED displays. One advantage of using polymeric materials rather than small molecules is the ease of deposition by spin-coating. For a monochrome display, only a metal cathode has to be deposited onto the polymer film. However, this technology poses a problem for multicolor displays: due to the spin-coating of the polymer film, it is difficult to obtain efficient light emission of multiple colors from a single polymer without further processing.

To solve this problem, several methods have been suggested to laterally pattern the polymer layer. Among these methods are conventional photolithography on top of the polymer layer⁴, photobleaching of dye⁵, plasma etching of the organic film and subsequent spin-coating of another polymer layer⁶, ink-jet printing of the polymer solution onto the substrate^{7,8} or printing a solution containing the dye onto a substrate which was previously deposited polymer film^{9,10}.

It has also been demonstrated that a large-area dye diffusion can locally change the emission color^{11,12}. In this case, the emissive dye is diffused into the spin-cast polymer layer from a large-area dye source. This dye source consists of a flat substrate coated with a layer containing the dye to be diffused. To pattern the polymer layer of the OLED, a shadow mask was placed in between the dye source and the device substrate during the diffusion process at elevated temperatures. Typical conditions to change the emission from blue to green or red are 40 min at 70 °C. However, due to the roughness of the steel shadow mask used in previous experiments (which was placed in intimate contact with the device substrate), the polymer film was often damaged resulting in short circuited devices. This paper will focus on recent progress to eliminate this shortcoming using either soft masks or a flat patterned dye source. In addition, a method for patterning the cathode layer will be introduced.

The OLED polymer film was deposited on a glass substrate coated with indium-tin-oxide (ITO) ($30 \Omega/\square$). The polymer used was poly(9-vinylcarbazole) (PVK, MW~ 1 100 000 g/mole, 71.5% by weight in the final solution) as the hole transport material and 2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (PBD, 28.5% by weight in the final solution) as the electron transport material¹³. Both, the PVK and the PBD, were obtained from Aldrich and used as received. The polymer blend also contained the dye 9,10-dioxa-*syn*-dimethylbimane (bimane, emission peak at 435 nm)¹⁴. The dyes diffused into the polymer film are coumarin 6 (C6, emission peak at 505 nm, obtained from Lambda Physik), and Nile red (emission peak at 580, obtained from Aldrich). Because the polymer blend contains already the blue dye, only two diffusion steps for the red and the green dye are required. The proposed processing of the OLED substrate is shown in Fig. 1. It should be noted that the electroluminescence (EL) emission of devices containing two or more dyes is almost entirely governed by the dye with the longest wavelength^{15,16}. Fig. 2 shows the photoluminescence (PL) and the electroluminescence (EL) spectra of a film spun-on from solution containing 100 mg PVK, 40 mg PBD and either 0.1 mg Nile red or 0.3 mg Nile red. Since the polymer blend also contains PBD, emission from PBD at 425 nm is detected. The PL spectra show a strong emission from PBD for both Nile red concentrations. However, in the EL spectra, the PBD emission is strongly quenched for the higher Nile red concentration, and the emission from Nile red dominated the spectrum. Similarly, Fig. 3 shows the PL and EL spectra for a device bimane and C6 for the dye concentrations of 0.3 mg bimane and 0.3 mg C6 in 100 mg PVK and 40 mg PBD. Again, in EL, the emission is only seen from the low bandgap dye.

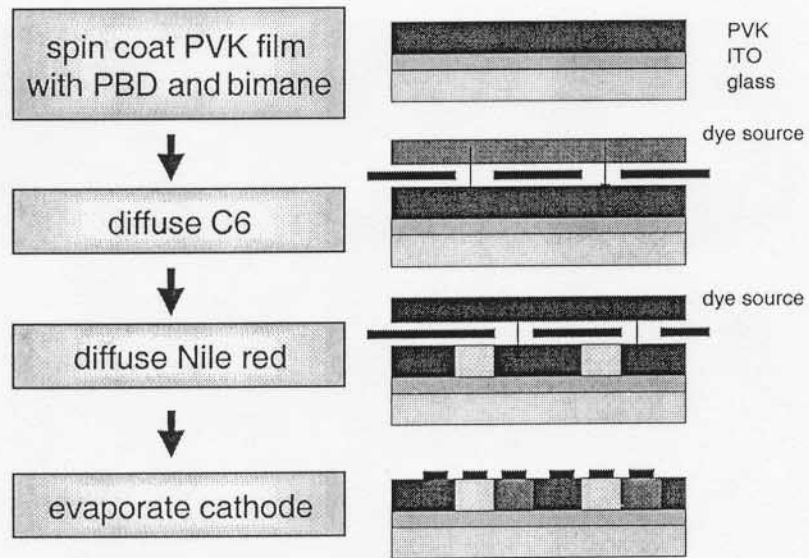


Fig. 1: Dye diffusion process for a 3-color polymer OLED

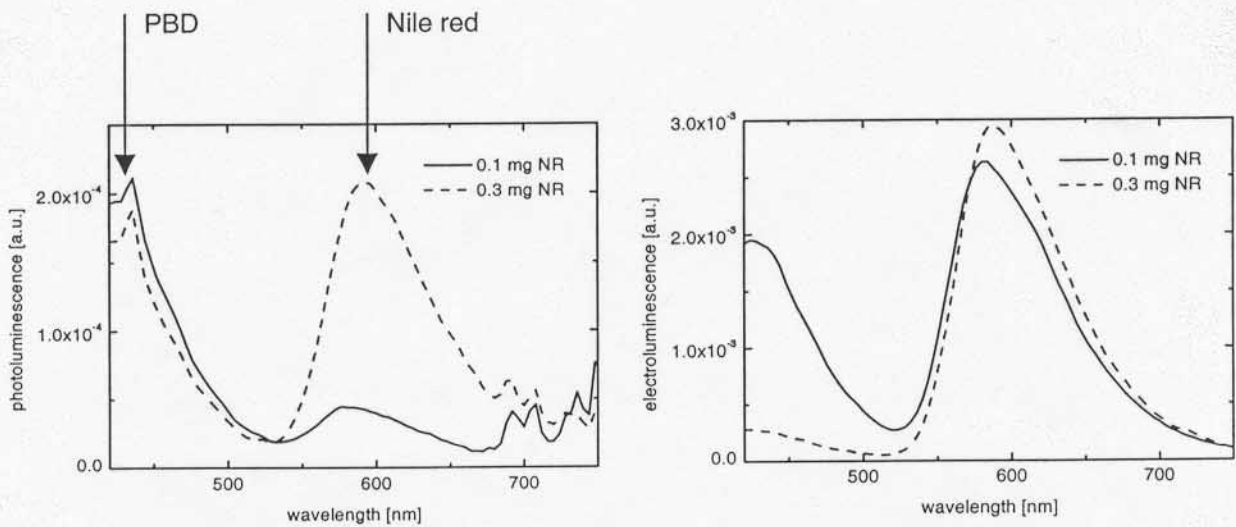


Fig. 2: Photoluminescence and electroluminescence spectra of PVK/PBD devices with either 0.1 mg Nile red or 0.3 mg Nile red spun-on from solution containing 100 mg PVK and 40 mg PBD. The PL pump wavelength was 215 nm.

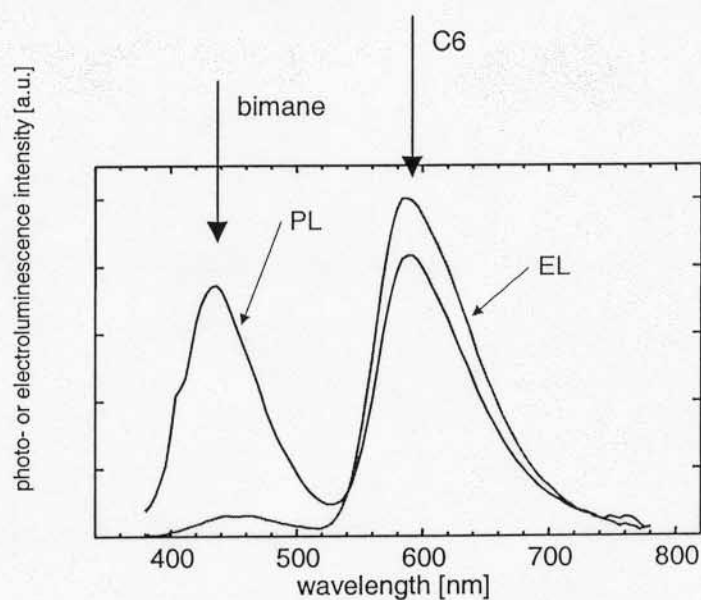


Fig. 3: Photoluminescence and electroluminescence spectra of PVK/PBD devices with 0.3 mg bimane and 0.3 mg C6 spun-on from solution containing 100 mg PVK and 40 mg PBD.

PHOTORESIST AS SHADOW MASK FOR DYE DIFFUSION

To avoid the described problems of damaging the polymer film of the OLED during the dye diffusion process, the use of soft masks of organic materials is desirable. However, because of the sensitivity of the dye containing film of the dye source to solvents and spin-on photoresist, direct patterning of the dye-source was not feasible. We therefore laminated a pre-patterned polymer layer onto the dye-source substrate to prevent any disturbance of the dye-source film. The pre-patterned polymer layer was formed using a commercially available photoresist (obtained from DuPont, trade name Riston CM 206). It consists of a 16 μm thick photosensitive layer, which is sandwiched in between two supporting transparent plastic foils. After conventional photolithographic exposure, one of these foils was removed, and the photoresist, still supported by one transparent foil, was developed, followed by drying at room temperature. This film was then laminated at 150 $^{\circ}\text{C}$ using a simple commercial laminator onto the dye-source, which consisted of a glass substrate and a previously spun-on dye-containing film. This process is illustrated in Fig. 4. The diffusion source for green and red emission was spin-cast from a solution containing 12 mg PVK and 50mg C6, or 13 mg PVK and 7mg Nile red, respectively. The masked dye source was then placed onto the polymer film of the device substrate. The diffusion process was carried out in vacuum at 70 $^{\circ}\text{C}$ for 40 min, with a pressure of 1500 Pa exerted on the dye-substrate. After the diffusion, the dye source/mask substrate was then separated from the OLED plate. For cathodes, the device substrate was coated with a Mg:Ag (10:1) cathode by thermal evaporation. The IV-characteristic, along with the measured photocurrent due to light emission, of a diffused device on a un-patterned substrate is shown in Fig. 5. In this experiment, we diffused C6 into a PVK/PBD layer (100 mg PVK, 40 mg PBD) using the same dye source as described above. The diffusion was carried out at 74 $^{\circ}\text{C}$ for 10 min. After the diffusion, the sample was annealed at 74 $^{\circ}\text{C}$ for 1 hour in vacuum. For comparison, two other devices were fabricated at the same time. Both of these samples were spun-on using a polymer solution, which already contained C6 (100 mg PVK, 40 mg PBD and 0.3 mg C6). One sample was coated with the metal cathode directly after the polymer deposition. The other sample was kept at 70 $^{\circ}\text{C}$ for 1 hour in vacuum before the deposition of the cathode. The annealed device shows no significant change in their IV or photocurrent. So we conclude that the heat treatment at 70 $^{\circ}\text{C}$ has little intrinsic effect on the materials system. The diffused device has a similar IV curve to the other devices, but a much lower photocurrent. We think that the decreased photocurrent is due to the lack of control of the amount of dye diffused into the polymer film.

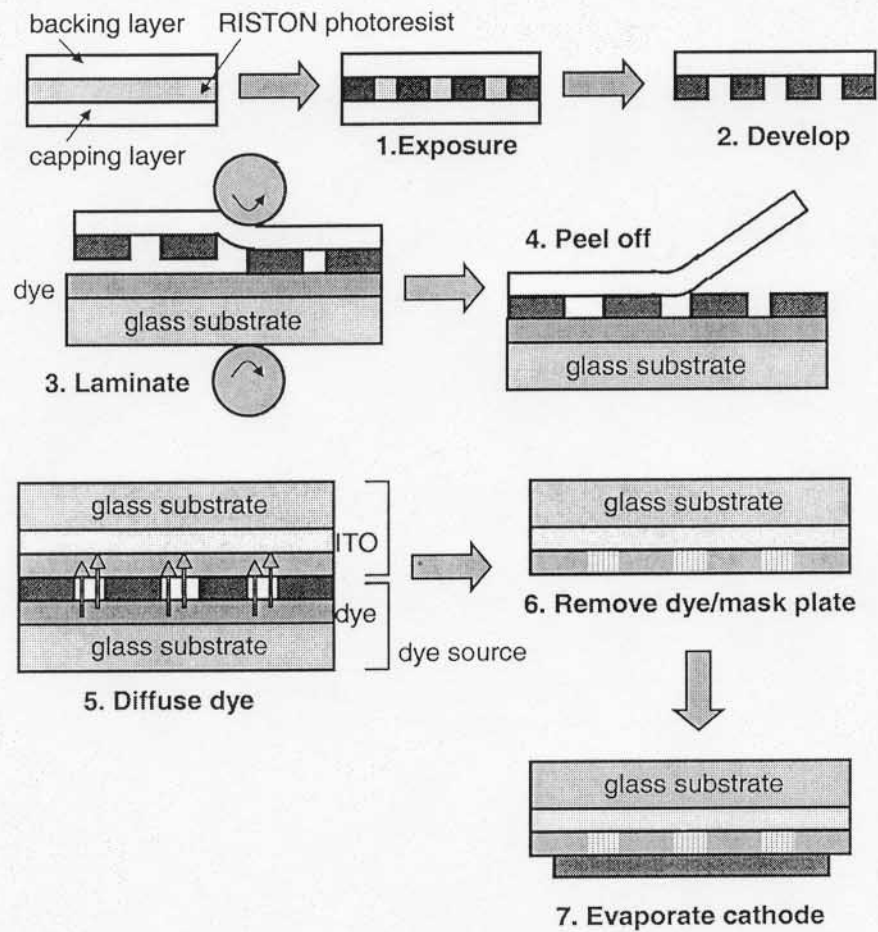


Fig. 4: Use of transferred photoresist as mask for dye diffusion.

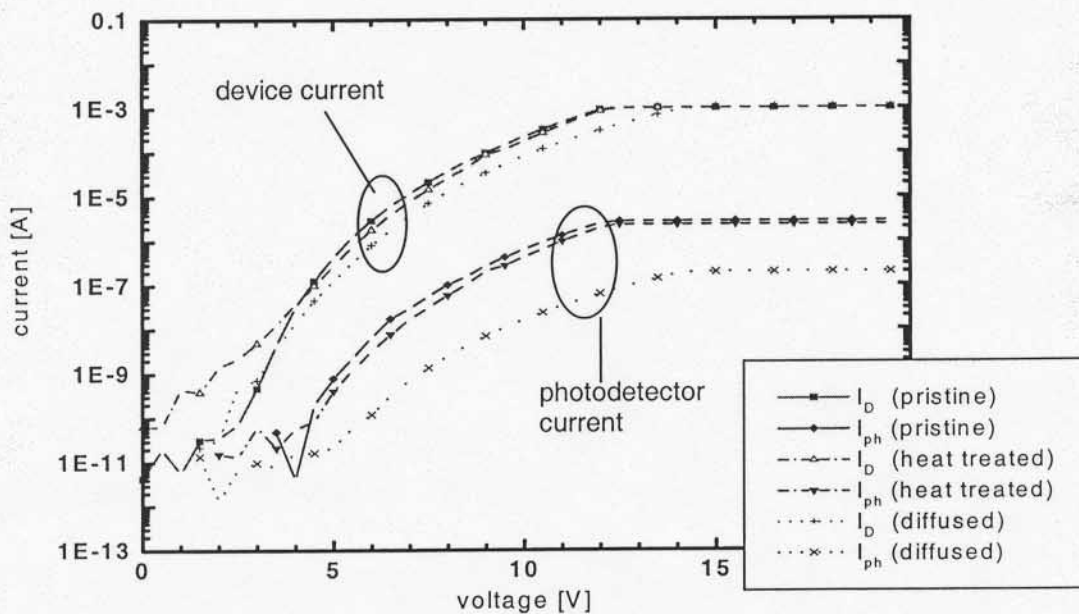


Fig. 5: IV-characteristics and photocurrents of different devices with emitting area of 2 mm^2 : (a) a device (PVK/PBD/C6) which was not exposed to heat at all, (b) a device (PVK/PBD/C6) which was kept at 70°C for 1 hour under vacuum, and (c) a device (PVK/PBD only) with diffused C6 and subsequent anneal for 1 hour at 74°C in vacuum.

In samples with a diffused pattern, lines of 20 μm width with a 40 μm pitch were observed by UV-excited fluorescence microscopy. The width was limited mainly by the resolution of the thick-film photoresist used (Fig. 6(a)). An EL micrograph of a different pattern fabricated with the same technology is shown in Fig. 6(b). No mechanical damage to the device was observed after the diffusion process. However, due to the contact of the photoresist with the polymer layer, a slight overall photoluminescence quenching was observed which occurred both in regions where the photoresist had been in contact with the device polymer film as well as in areas between the contact regions. Since the quenching may be due to out-diffusion of an undesired species in the photoresist, a process described in the next section was developed to avoid the presence of the resist during the diffusion cycle.

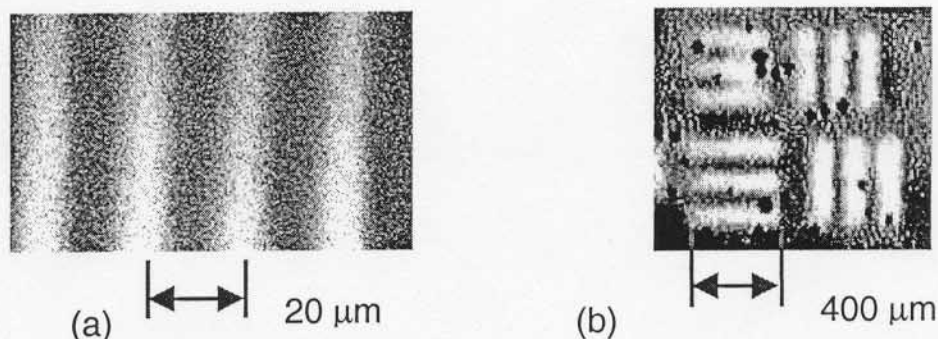


Fig. 6: (a) PL micrograph and (b) EL micrograph of lines with C6 diffused into a film of PVK/PBD using a transferred photoresist mask

DYE DIFFUSION USING A PATTERNED DYE SOURCE

To avoid any contact of the device polymer layer with any material other than the dye, we then used the laminated photoresist as an etching mask for the dye source. After the lamination of the photoresist onto the dye source (following the same steps described earlier), the substrate was treated with an oxygen plasma. This process removed all organic material, which was not covered with photoresist. To remove the photoresist after patterning the dye-source film, a cleaned aluminum foil was laminated onto the dye source plate, making contact with the thick photoresist. Because of the good adherence of the aluminum foil to the photoresist layer, the photoresist could be simply lifted off, leaving only islands of the dye-source film on a flat glass substrate. The patterned dye-source substrate was then put into close contact with the device substrate with a pressure of 1500 Pa as shown in Fig 7. The dye diffusion was carried out at 70 $^{\circ}\text{C}$ for 90 min in air.

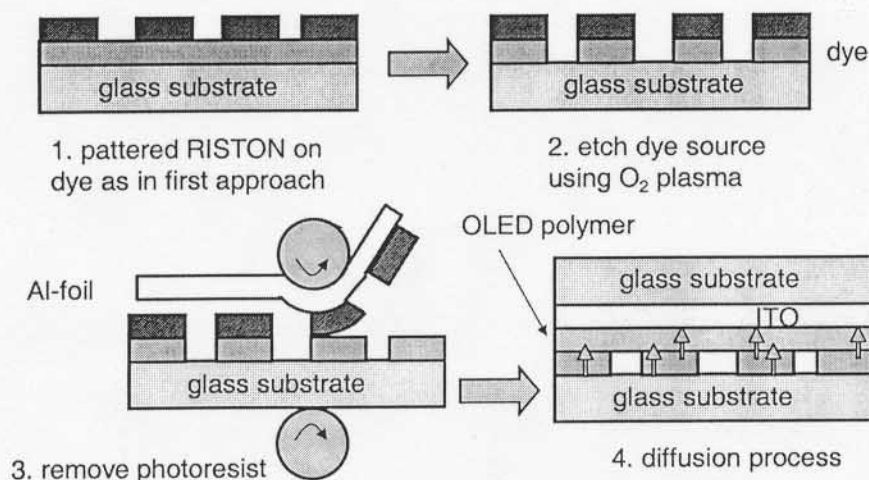


Fig. 7: Dye diffusion process using patterned dye substrate

Fig. 8 shows a micrograph of the electro-luminescence of a 3 mm high letter with 200 μm color features. The outline of the letter is defined by ITO, and a blanket Mg:Ag cathode was deposited. The 200 μm bright stripes are lines where the dye Nile red was diffused into the PVK/PBD film. The polymer film itself emits only very weakly in the blue.

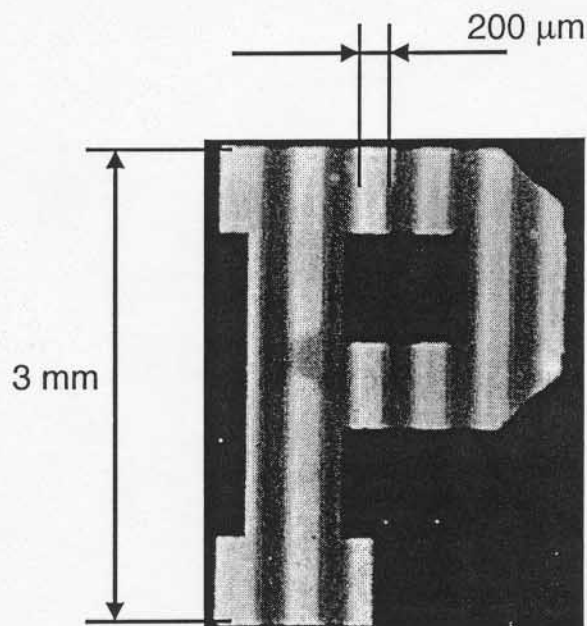


Fig. 8: EL micrograph of a 3 mm high letter with 200 μm lines of diffused Nile red

THERMAL DIFFUSION / STABILITY OF THE DYE PATTERN

Both for modelling the dye diffusion process and for the long-term stability of the device, it is of major importance to know the diffusion rate of the dye in the PVK/PBD film. It is expected that the rates are very high above the glass transition temperature T_g and very small below it^{17, 18}. For the PVK/PBD blend used in this experiment, T_g is approximately 125 $^{\circ}\text{C}$ ¹⁹. To investigate the stability, we diffused C6 with a pattern of 20 μm and 40 μm pitch into a PVK/PBD film at 70 $^{\circ}\text{C}$. The films were annealed and the change in PL vs. distance along the surface was used as evidence of lateral dye diffusion in the polymer. Initially, we observed anomalously high diffusion rates, which were found to be due to evaporation of dye, followed by gas phase transport and re-deposition onto undoped areas some distance away. To eliminate this effect, a 60 nm thick layer of SiNO_x at 50 $^{\circ}\text{C}$ by Plasma Enhanced Chemical Vapor Deposition (PECVD) was deposited on the polymer surface. This solved the anomalous diffusion problem, and also helped to reduce any polymer degradation due to contact with air and water vapor at the annealing temperature. The photoluminescence image was taken using a fluorescence microscope. The samples were then annealed for four hours at 90 $^{\circ}\text{C}$, 105 $^{\circ}\text{C}$, 120 $^{\circ}\text{C}$, or 135 $^{\circ}\text{C}$. After anneal, a PL image was taken at the same spot, and compared to the one taken before the anneal (Fig. 9). We were unable to detect any lateral diffusion of the dye at annealing temperatures below 120 $^{\circ}\text{C}$, but samples annealed at higher temperatures showed a slight lateral diffusion. By modelling the evolution of these profiles, the diffusion coefficient of dye was extracted and found to be $D = 7 \cdot 10^{-13} \pm 2 \cdot 10^{-13}$ cm^2/s for 120 $^{\circ}\text{C}$ and $D = 8 \cdot 10^{-12} \pm 4 \cdot 10^{-12}$ cm^2/s for 135 $^{\circ}\text{C}$.

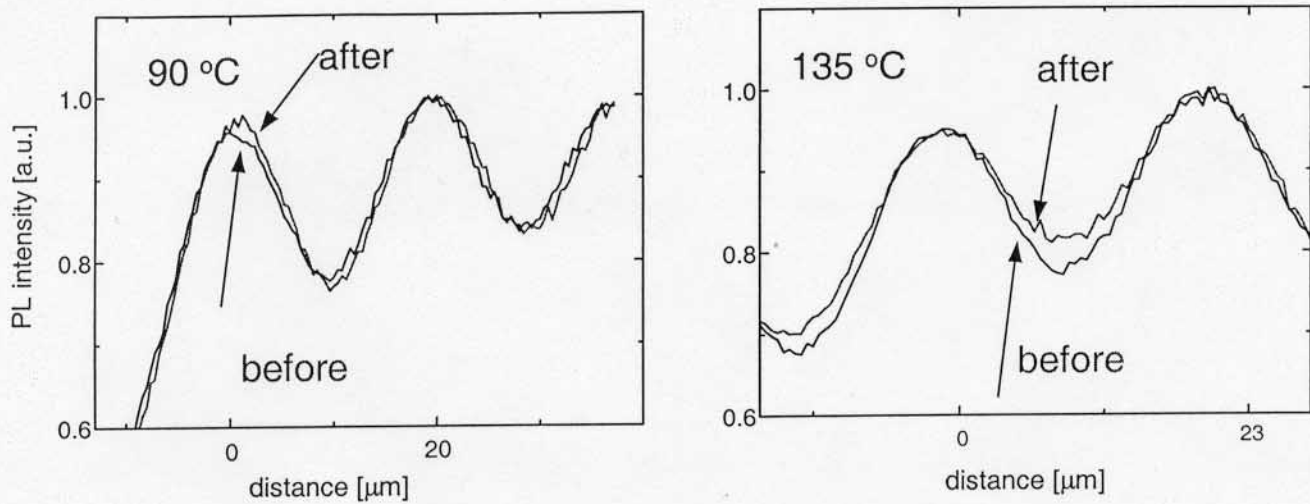


Fig. 9: Spatial PL intensity profiles before and after 4 hour anneal at 90 °C or 135 °C of substrates with C6 stripes patterns diffused into PVK/PBD film.

Because no change could be detected within experimental resolution at temperatures of 90 °C and 105 °C, an upper limit for the dye diffusion coefficient at these temperatures is 10^{-13} cm²/s. To more accurately predict the diffusion at lower temperatures, one needs a model with which one can extrapolate diffusion coefficients at 120 °C and 135 °C to lower temperatures. Diffusion in polymers is mainly dependent on the glass transition temperature of the polymer and the volume of the molecule diffused into the polymer film. Based on the free volume theory²⁰, the diffusion in polymer is controlled by the free space between the polymer strands, effectively forming cells, and the ability of the polymer to move in order to connect these cells and hereby enable the molecule to diffuse further in the polymer film. Since this theory is based on the movement at least parts of polymer chain, the model is only valid above the glass transition temperature of the polymer film. An empirical formula was developed by Williams *et al.* (WLF-equation)²¹ to describe the diffusion coefficient as a function of temperature²²:

$$\log D = \frac{c(T - T_g)}{51.5 + T - T_g} + \log D_g$$

where D_g is the diffusion constant at T_g and c is a polymer dependent constant. One can fit our data at 120 °C and 135 °C to yield a c of 4.7 (Fig. 10). However, this model is not valid below T_g - it produces a diverging diffusion coefficient at $T = T_g - 51.5$ °C. Further work is necessary to characterize dye diffusion at low temperatures.

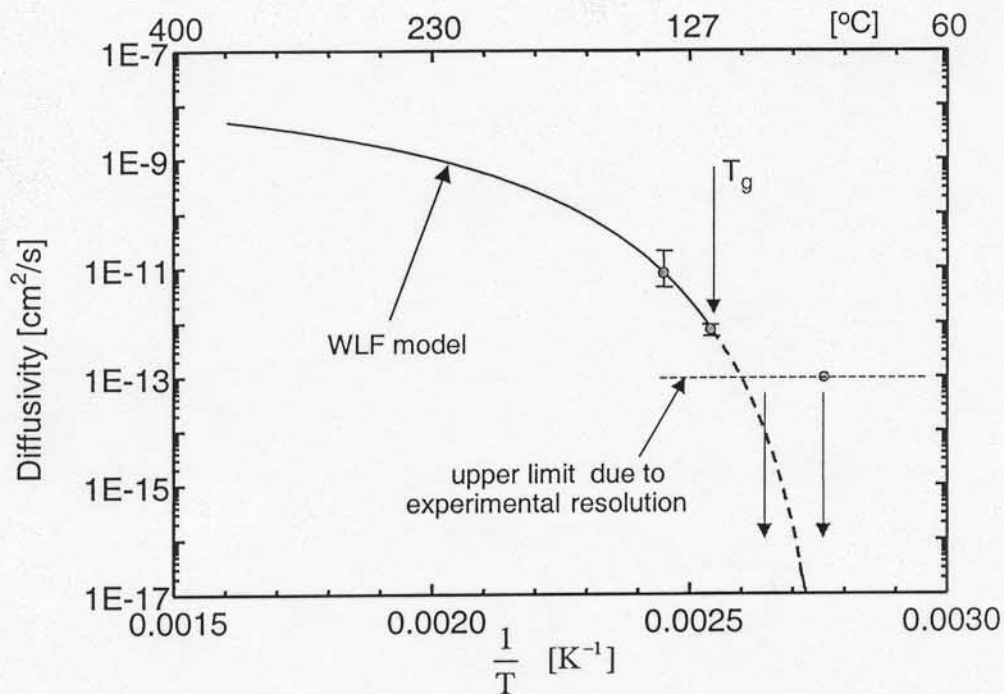


Fig. 10: Measured diffusivity D of C6 in PVK/PBD blend, and fit using the WLF-equation to points at 120 °C and 135 °C. The points at 90 °C and 105 °C are upper limits due to experimental resolution.

CATHODE PATTERNING AND INTEGRATED RGB DEVICE

To form metal lines in OLED matrices fabricated by small-molecule technology, a standard practice is to first photolithographically pattern pillars of a photo-processable material as cathode separators, before evaporating the organic materials and the metal cathode. However, for a polymer-based technology, spin-coating of polymers with existing cathode separators structures is a challenge. Patterning photoresist pillars on top of a polymer as cathode separators is difficult due to the incompatibility between the polymer and photoresist processing. Using the same technique of transferring a pre-patterned photoresist film onto the emissive layer, we were able to pattern the cathode layer without exposing the emissive layer to any solvents (Fig. 11). Fig. 12 shows an EL-micrograph of a device fabricated with this technology where the width of the cathode is 120 μm .

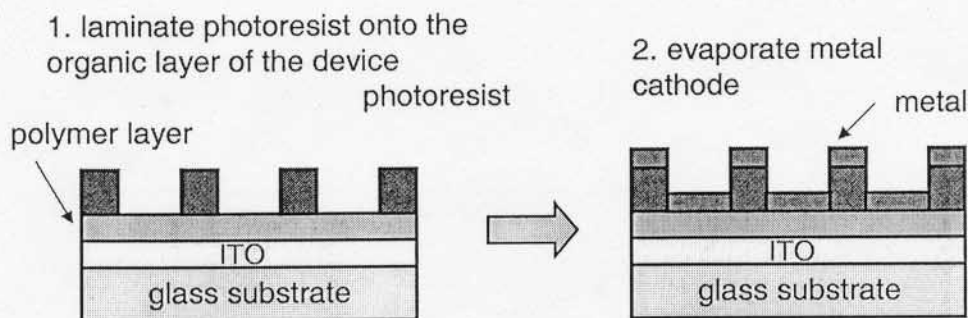


Fig. 11: Schematic process to form cathode separators using transferred photoresist

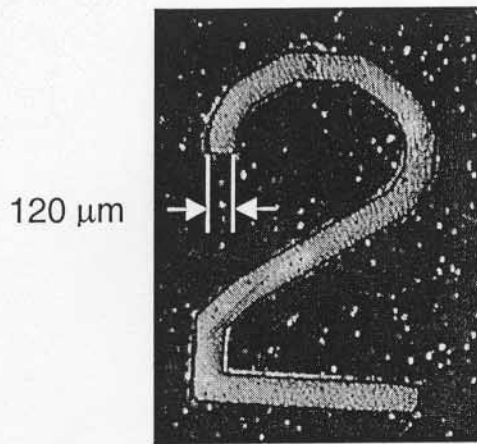


Fig. 12: EL micrograph of an OLED feature fabricated using transferred photoresist

The dye diffusion technique and the cathode patterning technique were used together to fabricate an integrated RGB device. On a glass substrate with ITO-lines, a PVK layer containing also PBD and bimane, the blue dye, was coated by spin-casting. After two diffusion processes using patterned dye diffusion sources for C6 and Nile red, a cathode separator was laminated onto the PVK layer, and the metal cathode lines were deposited. Devices were formed at the intersection of the ITO-lines and the cathode metal lines. Fig. 13 shows a device with three LEDs each 0.5 mm by 0.5 mm. All diodes could be turned on independently and emitted in the blue, red, and green, respectively.

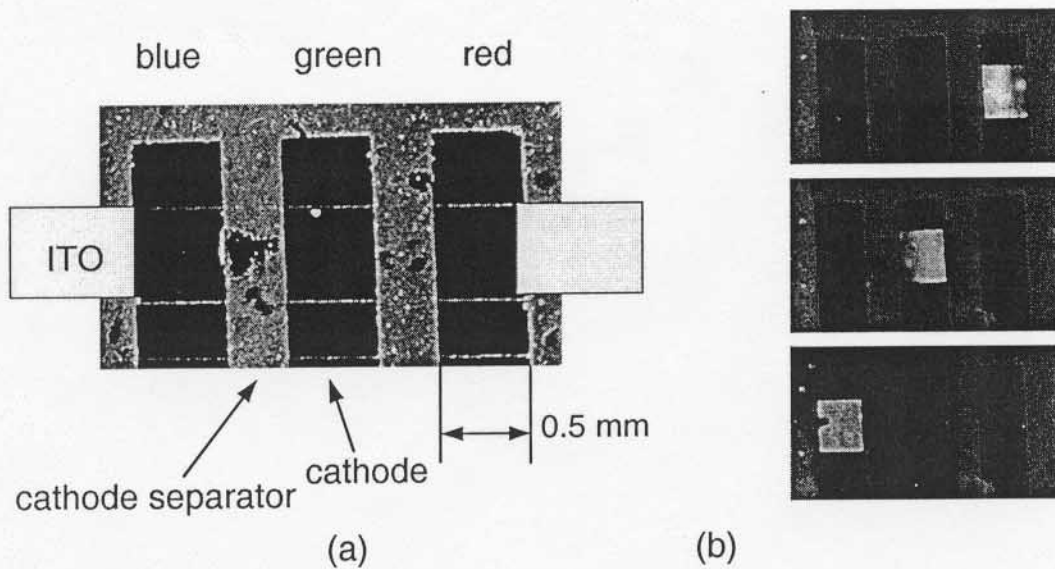


Fig. 13: (a) Top view of integrated device structure after diffusion of color columns and formation of cathode separators, and (b) independent operation of RGB devices

CONCLUSION

In conclusion, we have demonstrated a photoresist transfer technology, which allows one to locally change the emissive color of an OLED by using large-area dye diffusion without damaging the emissive layer. In addition, the technology can also be applied to pattern the metal cathode, and is attractive for the formation of color OLED displays. Further work is necessary to understand the mechanisms of the dye diffusion, and to understand the dependence of device performance on dye concentration.

ACKNOWLEDGEMENT

This work was supported by DARPA, NSF and NJCST.

REFERENCES

1. A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, and E. P. Woo, "High brightness and efficiency blue light-emitting polymer diodes," *Appl. Phys. Lett.* **73**, pp. 629 - 631, 1998.
2. S. E. Shaheen, G. E. Jabbour, B. Kippelen, N. Peyghambarian, J. D. Anderson, S. R. Marder, N. R. Armstrong, E. Bellmann, and R. H. Grubbs, "Organic light-emitting diode with 20 lm/W efficiency using a triphenyldiamine side-group polymer as the hole transport layer," *Appl. Phys. Lett.* **74**, pp. 3212 - 3214, 1999.
3. J. Kido and Y. Iizumi, "Fabrication of highly efficient organic electroluminescent devices," *Appl. Phys. Lett.* **73**, pp. 2721 - 2723, 1998.
4. D. G. Lidzey, M. S. Weaver, D. D. C. Bradley, M. A. Pate, T. A. Fisher, "Photoprocessed and micropatterned conjugated polymer LEDs," *Synthetic Metals* **83**, pp. 141-148, 1996.
5. J. Kido, presented at *Symp. Mat. Res. Soc.*, San Francisco, CA, April 1999.
6. C. C. Wu, J. C. Sturm, R. A. Register, and M. E. Thompson, "Integrated three-color organic light-emitting devices," *Appl. Phys. Lett.* **69**, pp. 3117 - 3119, 1996.
7. T. R. Hebner, C. C. Wu, D. Marcy, M. H. Lu, and J. C. Sturm, "Ink-jet printing of doped polymers for organic light emitting devices," *Appl. Phys. Lett.* **72**, pp. 519-521, 1998.
8. T. Shimoda, S. Kanbe, H. Kobayashi, S. Seki, H. Kiguchi, I. Yudasaka, M. Kimura, S. Miyashita, R. H. Friend, J. H. Burroughes, and C. R. Towns, "Multicolor Pixel Patterning of Light-Emitting Polymers by Ink-Jet Printing," *SID conference*, San Diego, CA, 1999.
9. T. R. Hebner and J. C. Sturm, "Local tuning of organic light-emitting diode color by dye droplet application," *Appl. Phys. Lett.* **73**, pp. 1775 - 1777, 1998.
10. J. Bharathan and Y. Yang, "Polymer electroluminescent devices processed by inkjet printing: Polymer light-emitting logo," *Appl. Phys. Lett.* **72**, pp. 2660 - 2662, 1998.
11. F. Pschenitzka and J. C. Sturm, "Three-color organic light-emitting diodes patterned by masked dye diffusion," *Appl. Phys. Lett.* **74**, pp. 1913 - 1915, 1999.
12. K. Tada and M. Onoda, "Three-Color Polymer Light-Emitting Devices Patterned by Maskless Dye Diffusion onto Prepatterned Electrodes," *Jpn. J. Appl. Phys.* **38**, pp. L 1143 - 1145, 1999.
13. C. C. Wu, J. C. Sturm, R. A. Register, J. Tian, E. P. Dana, and M. E. Thompson, "Efficient Organic Electroluminescent Devices Using Single-layer Doped Polymer Thin Films with Bipolar Carrier Transport Abilities," *IEEE Trans. Electron Devices* **44**, pp. 1269, 1997.
14. T. G. Pavlopoulos, C. J. McBee, J. H. Boyer, I. R. Politzer, and C. M. Lau, "Laser action from syn-(methyl,chloro)bimane," *J. Appl. Phys.* **62**, pp. 36, 1987. The bimane was supplied by M. E. Thompson at ULCA.
15. J. Kalinowski, P. D. Marco, V. Fattori, L. Giulietti, and M. Cocchi, "Votage-induced evolution of emission spectra in organic light-emitting diodes," *J. Appl. Phys.* **83**, pp. 4242 - 4248, 1998.
16. F. Pschenitzka and J. C. Sturm, "Three-Color Doping of Polymer OLEDs by Masked Dye Diffusion," *Materials Research Society Symposium Proceedings*, B. R. Chalamala, R. H. Friend, T. N. Jackson, and F. R. Libsch **558**, pp. 513 - 518, Material Research Society, San Francisco, 1999.
17. A. T. Slark and P. M. Haddgett, "The effect of specific interactions on dye transport in polymers above the glass transition," *Polymer* **40**, pp. 4001 - 4011, 1999.
18. J. C. Selsler, "Diffusion of Dye Molecules in Polymers above and below the Glass transition Temperature Studies by Holographic Grating Technique," *Macromolecules* **18**, pp. 587 - 589, 1985.
19. Personal communication: Xuezhong Jiang and R. A. Register, July 2000.
20. C. A. Kumins and T. K. Kwei, "Free Volume and Other Theories," *Diffusion in Polymers*, J. Crank, and G. S. Park, pp. 107 - 140, New York, 1968.
21. M. L. Williams, R. F. Landel, and J. D. Ferry, "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids." *Am. Chem. Soc.* **77**, 3701 - 3707, 1955.
22. T. E. Shearmur, D. W. Drew, A. S. Clough, M. G. D. v. d. Grinten, and A. T. Slark, "Study of dye diffusion using Rutherford backscattering," *Polymer* **37**, pp. 2695 - 700, 1996.